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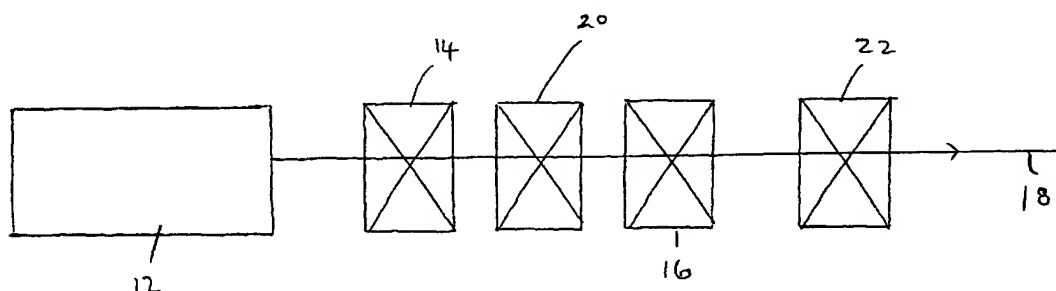
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(54) Title: EXHAUST SYSTEM FOR A DIESEL ENGINE COMPRISING A NO_x-TRAP



(57) Abstract: An exhaust system (10) for a diesel engine (12) comprises a first NO_x-trap (16) comprising at least one first NO_x absorbent and platinum, characterised in that at least one second NO_x absorbent (14) is disposed upstream of the first NO_x trap, which at least one second NO_x absorbent is not associated with platinum

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WO 2004/030798 A1

EXHAUST SYSTEM FOR A DIESEL ENGINE COMPRISING A NO_x-TRAP

5 The present invention relates to an exhaust system for a diesel engine, which system comprising a first nitrogen oxide (NO_x)-trap comprising at least one first NO_x absorbent and platinum.

10 Exhaust gases from compression ignition engines, such as diesel engines, comprise a mixture of pollutants including carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM) including volatile and soluble organic fractions (VOF and SOF respectively). The NO_x component can comprise nitrogen monoxide (NO) and nitrogen dioxide (NO₂). The level of these pollutants in exhaust gases from internal combustion engines it is permissible to exhaust
15 to atmosphere is regulated by legislation. Such legislation can be met by engine design, engine management and/or exhaust gas after treatment, and typically a combination of all three measures.

20 In conventional diesel engines, present legislated limits for HC and CO can be met using a platinum (Pt)-based diesel oxidation catalyst (DOC). Diesel nitrogen oxides (NO_x) emissions are presently controlled by engine management, such as exhaust gas recirculation (EGR). As a consequence, however, PM emissions including VOF and SOF are increased. The DOC is used to treat VOF and SOF in order to meet presently legislated limits for PM.

25

 Another prior art exhaust system primarily for treating diesel exhaust comprises an oxidation catalyst for oxidising NO in the exhaust gas to NO₂ and a downstream filter for trapping PM. A process for treating diesel PM that uses this arrangement is described in EP 0341382 or US patent no. 4,902,487, both of which are incorporated
30 herein by reference. The process comprises passing diesel exhaust gas including PM and NO unfiltered over an oxidation catalyst to convert the NO to NO₂, collecting soot on the filter and combusting the collected soot by reaction with the NO₂. This technology is commercially available as Johnson Matthey's Continuously Regenerating Trap or CRT®. Combustion of the PM in NO₂ results in CO and NO, with a potential side-reaction
35 leading to the complete reduction of the NO₂ to N₂ as described in SAE 890404.

A problem with the process described in EP 0341382 and in the use of exhaust gas after treatment catalysts such as DOC is that, as exhaust emission legislation is tightened, legislative bodies have begun to discuss limiting the amount of NO₂ it is permissible to exhaust to atmosphere. For example, the California Air Resources Board (CARB) has proposed that a maximum of 20% of tailpipe NO_x of the relevant drive cycle is emitted as NO₂ (see CARB's Diesel Risk Reduction Program and Final Regulation Order Chapter 14 "Verification procedure, warranty and in-use compliance requirements for in-use strategies to control emissions from diesel engines", section 2706). NO₂ is toxic and can cause headaches, dizziness and nausea in low doses. It also has an objectionable smell. In the process of EP 0341832, if there is insufficient PM on the filter to react with NO₂ generated over the oxidation catalyst or the temperature of the exhaust gas is below a preferred range for combustion of PM in NO₂, NO₂ can slip past the filter and be undesirably exhausted to atmosphere.

At low exhaust gas temperatures, e.g. about 200-250°C, and part-load, a modern diesel engine produces a relatively high amount of NO_x in the form of NO₂. If, as is typical in an exhaust system for a lean-burn internal combustion engine including a NO_x-trap, the exhaust gas is first passed over a platinum oxidation catalyst, the NO₂ can be removed by facile low temperature oxidation of hydrocarbons present in the exhaust gas. This process is known as lean NO_x catalysis. In any event, the NO_x absorbent material can poison the lean NO_x activity of the platinum, thereby reducing the conversion efficiency of the process. At higher temperatures, e.g. above about 300-350°C, the oxidation of NO to NO₂ becomes sufficiently rapid for significant quantities of NO₂ to be formed and a conventional platinum containing NO_x-trap then starts to become effective.

A NO_x-trap is purposely designed for absorbing and storing NO_x in lean exhaust gases ($\lambda > 1$ conditions), and releasing and catalytically reducing the stored NO_x in rich exhaust gases ($1 > \lambda$ conditions). To remove the stored NO_x, typically the engine is controlled so that periodically it is run rich during normal lean-running operation. A NO_x-trap typically includes active materials for three functions: an oxidation catalyst, such as platinum; a NO_x absorbent, for example a compound of an alkali metal e.g. a potassium and/or a caesium, an alkaline earth compound typified by

barium oxide or a compound of a rare earth metal, such as lanthanum; and a reduction catalyst, such as rhodium. In the exhaust gas the or each alkali metal and alkaline earth metal compound is present as an oxide, although it may also be present in use as a hydroxide or a carbonate.

5

A convention used herein is to refer to a "NO_x-trap" as a composition comprising a NO_x absorbent and at least one catalytic material, such as a platinum group metal. NO_x absorbent refers to a material, e.g. alkaline earth metal compound, alkali metal compound or rare earth metal compound, capable of absorbing NO₂ in lean exhaust gas.

10

An oxidation catalyst is purposely designed to provide for the reaction of gaseous components with oxygen, typically in as wide a temperature range as possible, especially at lower temperatures. The catalyst oxidises whenever oxygen is available for reaction in the gas stream. Active components of an oxidation catalyst can include platinum, palladium or a base metal active for oxidation such as manganese, copper, molybdenum, cobalt or any other transition element that is active for oxidation.

15

An oxygen storage component (OSC) is purposely designed to absorb oxygen from lean exhaust gases and to release oxygen in rich exhaust gas conditions. Examples of suitable OSC include ceria doped with transition metals, e.g. zirconium, or other rare earth metals and manganese-based materials.

20

According to the present specification, "adsorb" and "absorb" in relation to the storage of NO_x on suitable basic materials have the same meaning.

25

Our WO 02/18753 (incorporated herein by reference) describes an exhaust system for a lean-burn internal combustion engine, including a diesel engine, comprising an oxidation catalyst upstream of a NO_x-trap for oxidising relatively large amounts of unburned hydrocarbons present in exhaust gas in normal lean-running conditions and for oxidising NO in the exhaust gas to NO₂ in lean-running conditions. In one embodiment, a clean-up catalyst comprising an oxygen storage component such as ceria, an oxidation component, such as platinum, a NO_x reducing component, for example rhodium, and a

30

component for suppressing H_2S , for example NiO , Fe_2O_3 , MnO_2 , CoO and CrO_2 , is disposed downstream of the NO_x -trap.

In WO 01/94760, we disclose an exhaust system for a diesel engine comprising a solid NO_x absorbent for absorbing NO_x from relatively cool exhaust gas and desorbing adsorbed NO_x and passing it to atmosphere by intermittently increasing the temperature of the exhaust gas.

We have now found that by using a NO_x -absorbent which is free of platinum to absorb relatively low temperature engine-derived NO_2 upstream of a NO_x -trap comprising platinum when the NO_x -trap is too cool to catalytically reduce the NO_2 to N_2 and to thermally release stored NO_x when the NO_x reducing function of the NO_x -trap is up to temperature, the exhaust system as a whole is able to treat NO_x more efficiently. More particularly, we have found that the system slips less NO_2 to atmosphere than a system comprising a conventional NO_x -trap comprising a NO_x absorbent and platinum as the sole NO_x absorbent-containing component.

According to one aspect, the invention provides an exhaust system for a diesel engine, which system comprising a first NO_x -trap comprising at least one first NO_x absorbent and platinum, characterised in that at least one second NO_x absorbent is disposed upstream of the first NO_x -trap, which at least one second NO_x absorbent is not associated with platinum.

A further advantage of this system over the above-mentioned prior art system is that the system of the invention generates less N_2O by lean NO_x catalysis over the platinum component of the first NO_x -trap.

An aspect of the present invention is the concept of absorbing NO_2 on the second NO_x absorbent at relatively low temperature when the downstream first NO_x trap is too cool to catalyse the reduction of NO_x to N_2 , and thermally releasing the NO_x when the first NO_x -trap is up to temperature, e.g. $>200^\circ\text{C}$, such as $>225^\circ\text{C}$, $>250^\circ\text{C}$, $>275^\circ\text{C}$ or $>300^\circ\text{C}$.

As is typical for engines including exhaust systems comprising NO_x-traps, the engine can include an engine control unit (ECU) programmed, in use, intermittently to adjust to the exhaust gas composition to the rich side for regenerating the at least one first NO_x absorbent.

5

Whilst the at least one second NO_x-absorbent can be associated with a base metal catalyst, e.g. a manganese compound, a cobalt compound or a copper compound, for oxidising nitrogen monoxide (NO) to nitrogen dioxide (NO₂) in lean exhaust gas or a non-platinum platinum group metal, such as rhodium or iridium for reducing NO_x to N₂ in rich exhaust gas, or other non-platinum PGMs such as palladium, osmium and ruthenium, preferably the at least one second NO_x-absorbent is free from components other than the NO_x-absorbent and optional support.

Each first and second NO_x absorbent can be selected from alkaline earth metal compounds, alkali metal compounds or rare-earth metal compounds. Suitable alkaline earth metals include calcium, magnesium, strontium and barium. Alkali metals can be potassium and/or caesium and rare earth metals can be cerium, yttrium or praseodymium.

The first and second NO_x absorbent can be supported on a suitable support, such as particulate alumina, silica, zirconia, titania, ceria or a mixture or composite oxide according to any two or more thereof, such as ceria-zirconia or alumina-silica

"Composite oxide" as defined herein means a largely amorphous oxide material comprising oxides of at least two elements which are not true mixed oxides consisting of the at least two elements.

Alternatively, the NO_x-absorbent can comprise the support e.g. ceria *per se* or alumina *per se*.

30

In use, compounds according to the invention can be oxides, although they may be present as nitrates, hydroxides or carbonates in exhaust gas containing NO_x, CO and H₂O.

The first NO_x-trap can be coated on a flow-through monolith, but in one embodiment, it is coated on a particulate filter. In a further embodiment according to the latter aspect, the particulate filter can include a DOC, optionally comprising supported platinum and/or palladium. Alternatively, the first NO_x trap can be disposed downstream
5 of the filter, which arrangement adopting the process of EP 0341832 and disclosed in EP 0758713.

Optionally there may be a catalyst for oxidising NO to NO₂, such as platinum on an alumina support, disposed between the at least one second NO_x absorbent and the first
10 NO_x-trap as described in our WO 02/18753.

During NO_x-trap regeneration, pulses of rich exhaust gas can be produced by the engine to convert stored NO_x to nitrogen. During this process, hydrocarbon or carbon monoxide could pass through the system to atmosphere. To prevent this, the gas
15 downstream of the first NO_x-trap can be passed over an oxidation catalyst comprising an oxygen storage component, so even if the gas is overall reducing, reductants can still be oxidised, and prevented from entering the atmosphere. In one embodiment, the oxidation catalyst comprises platinum or palladium supported on a bulk ceria-zirconia composite oxide oxygen storage component.

20 According to a further aspect, the invention provides a diesel engine, optionally a light-duty diesel engine (as defined by the relevant legislation) comprising an exhaust system according to the invention.

25 According to a further aspect the invention provides a flow-through substrate comprising a NO_x-trap comprising a first zone coated with a composition comprising at least one first NO_x absorbent and platinum and a second zone coated with a composition comprising at least one second NO_x-absorbent, which at least one second NO_x absorbent is not associated with platinum.

30 According to a further aspect, the invention provides a method of treating NO_x in the exhaust gas of a diesel engine, which method comprising (i) absorbing NO₂ from lean exhaust gas in at least one second NO_x absorbent when a downstream first NO_x-trap

comprising at least one first NO_x absorbent and platinum is inactive for reducing NO_x using a suitable reductant; (ii) thermally desorbing stored NO_x; and (iii) reducing thermally desorbed NO_x on the first NO_x-trap using a suitable reductant.

- 5 In one embodiment, the method comprises the step between steps (i) and (ii) of adsorbing thermally desorbed NO_x on the at least one first NO_x absorbent.

10 In order that the invention may be more fully understood, the following embodiment and Examples are provided by way of illustration only and by reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of a diesel engine comprising an exhaust system according to the invention;

- 15 Figure 2 is a trace of time against NO₂ concentration (ppm) and temperature showing the experimental conditions used in the Examples;

20 Figure 3 is a trace showing NO₂ adsorption and desorption for a conventional NO_x trap comprising 5:1 Pt:Pd at a total loading of 120gft⁻³(4.25g litre⁻¹);

Figure 3A is a trace showing HC detected downstream of the NO_x absorbent in the experiment shown in Figure 3;

- 25 Figure 4 is a trace showing NO₂ adsorption and desorption for a washcoat component containing Pt at a loading of 80gft⁻³;

Figure 4A is a trace showing HC detected downstream of the NO_x absorbent in the experiment shown in Figure 4;

- 30 Figure 5 is a trace showing NO₂ adsorption and desorption for the washcoat component of the Figure 4 material without platinum;

Figure 5A is a trace showing HC detected downstream of the NO_x absorbent in the experiment shown in Figure 5.

In the exhaust system 10 shown in Figure 1, 12 is a diesel engine; 14 is a Pt-free NO_x-trap comprising a second NO_x-absorbent, e.g. alumina, barium supported on alumina or ceria; 16 is a NO_x-trap comprising a first NO_x-absorbent, such as barium supported on alumina, platinum and rhodium; 18 is the exhaust tailpipe. Optional components include an oxidation catalyst 20, such as platinum on alumina, and/or an oxidation catalyst 22 comprising an OSC, such as ceria-zirconium composite oxide.

We believe that Figure 1 is self explanatory, in combination with the above description.

EXAMPLE 1

A ceramic flow through monolith 1.5 inch (38mm) diameter and 3 inches (76mm) long was coated with a conventional NO_x-trap formulation containing platinum and rhodium at a ratio of 5:1 and total loading of 120gft⁻³ (4.25g litre⁻¹) and a barium on alumina NO_x-absorbent. The catalyst was fitted into a standard gas flow rig and a synthetic gas mixture passed over it at a space velocity of 30,000hr⁻¹. The gas mixture composition is shown in Table 1 and remained lean for all the tests.

Table 1 Synthetic Gas Mixture used for Tests

Gas	Concentration
NO ₂	200 or 250ppm
CO	0.05%
CO ₂	6%
H ₂ O	6%
O ₂	15%
C ₃ H ₆ (C1)	300ppm
N ₂	Balance

The gas mixture (without NO₂) flowing through the catalyst was heated to 500°C and held at this temperature for 5 minutes in order to purge the catalyst. The gas was allowed to cool to 120°C and held at this temperature while the NO₂ was added for a period of 5 minutes. The NO₂ was switched off and the gas temperature increased to 500°C for 5 minutes to purge the catalyst (Fig 2). Throughout the test the NO and NO_x/NO₂ at the outlet to the catalyst was continuously measured so that adsorption (storage) and desorption could be monitored (Fig 3).

From Fig. 3 it can be seen that there was some storage of NO₂ at low temperatures on this NO_x trap. The majority of the NO₂ entering the catalyst was converted to NO, which was not adsorbed by the storage component in the NO_x trap. When the temperature was increased NO_x began to desorb at 430°C and was complete at 500°C. When NO₂ was absent from the gas feed, hydrocarbons (HC) were oxidised over Pt sites, but when the NO₂ was introduced the HC reacted preferentially with it partially reducing it to NO (Fig 3A).

EXAMPLE 2

A washcoat, containing Pt, was coated onto a monolith, as in Example 1, to give a loading of 2.5g in⁻³ (0.15g cm⁻³) with a Pt loading of 80gft⁻³ (2.82g litre⁻¹) and evaluated as in Example 1. The results (shown in Fig 4) show that NO₂ was not stored at 120°C, but was all converted to NO by reaction with HC (Fig 4A).

EXAMPLE 3

The same washcoat, but excluding Pt, as used in Example 2 was coated on the same size monolith to give a loading of 2.5g in⁻³ (0.15g cm⁻³) and evaluated in the same way. The results show (Fig 5) that the Pt free washcoat stored NO₂. Considerably less NO₂ was reduced to NO than with the equivalent washcoat containing Pt, confirmed by the lower HC conversion (Fig 5A). Desorption of NO_x began as the temperature increased to 350°C.

The results show that the Pt free washcoat system stored the most NO₂ which was then desorbed at a sufficiently high temperature to ensure a Pt containing NO_x trap fitted downstream would be at its working temperature.

5 From these results, it appears that Pt free adsorber does not catalyse the reaction between HC and NO₂, reducing NO₂ to NO, to the same extent as a formulation containing Pt. NO₂ is more easily adsorbed than NO leading to an advantage for NO₂ adsorption of a Pt free adsorber at temperatures where the NO oxidation reaction is slow over Pt.

10

Similar results to those shown in Example 3 were obtained from a barium on alumina NO_x absorbent material.

CLAIMS:

1. An exhaust system for a diesel engine, which system comprising a first NO_x-trap comprising at least one first NO_x absorbent and platinum, characterised in that at least
5 one second NO_x absorbent is disposed upstream of the first NO_x-trap, which at least one second NO_x absorbent is not associated with platinum.
2. An exhaust system according to claim 1, wherein each first and second NO_x-absorbent is selected from the group consisting of alkaline earth metal compounds,
10 alkali metal compounds and rare earth metal compounds.
3. An exhaust system according to claim 2, wherein the or each alkaline earth metal is barium, magnesium, strontium or calcium.
- 15 4. An exhaust system according to claim 2, wherein the or each alkali metal is potassium or caesium.
5. An exhaust system according to claim 2, wherein the or each rare earth metal is cerium, yttrium, lanthanum or praseodymium.
20
6. An exhaust system according to claim 2, 3, 4 or 5, wherein the or each alkaline earth metal compound, the or each alkali metal compound or the or each rare earth metal compound is supported on a support material.
- 25 7. An exhaust system according to claim 6, wherein the or each support is alumina, silica, titania, zirconia, ceria or a mixture or composite oxide of any two or more thereof.
8. An exhaust system according to claim 6, wherein the NO_x absorbent comprises the support.
30
9. An exhaust system according to claim 1, wherein the second NO_x absorbent is alumina *per se*.

10. An exhaust system according to any preceding claim, further comprising a catalyst for oxidising NO to NO₂ disposed between the at least one second NO_x absorbent and the first NO_x-trap.

5 11. An exhaust system according to claim 10, wherein the NO oxidation catalyst is platinum on an alumina support.

12. An exhaust system according to claim 10 or 11, comprising a particulate filter disposed between the oxidation catalyst and the first NO_x-trap.

10

13. An exhaust system according to any of claims 1 to 11, wherein the first NO_x-trap comprises a particulate filter.

14. An exhaust system according to any preceding claim, further comprising a catalyst comprising a catalyst component for oxidising hydrocarbon and carbon
15 monoxide to water and carbon dioxide and an oxygen storage component, which catalyst is disposed downstream of the first NO_x-trap.

15. An exhaust system according to claim 14, wherein the oxidation catalyst
20 comprises platinum or palladium supported on a bulk ceria-zirconia mixed oxide oxygen storage component.

16. A diesel engine comprising an exhaust system according to any preceding claim.

25 17. A light-duty diesel engine according to claim 16.

18. An engine according to claim 16 or 17, comprising an engine control unit, when in use, intermittently to adjust the exhaust gas composition to the rich side for regenerating the at least one first NO_x absorbent.

30

19. A flow-through substrate comprising a NO_x-trap comprising a first zone coated with a composition comprising at least one first NO_x absorbent and platinum and a

second zone coated with a composition comprising at least one second NO_x-absorbent, which at least one second NO_x absorbent is not associated with platinum.

20. A method of treating NO_x in the exhaust gas of a diesel engine, which method comprising (i) absorbing NO₂ from lean exhaust gas in at least one second NO_x absorbent when a downstream first NO_x-trap comprising at least one first NO_x absorbent and platinum is inactive for reducing NO_x using a suitable reductant; (ii) thermally desorbing stored NO_x; and (iii) reducing thermally desorbed NO_x on the first NO_x-trap using a suitable reductant.

21. A method according to claim 20, comprising the step between steps (i) and (ii) of adsorbing thermally desorbed NO_x on the at least one first NO_x absorbent.

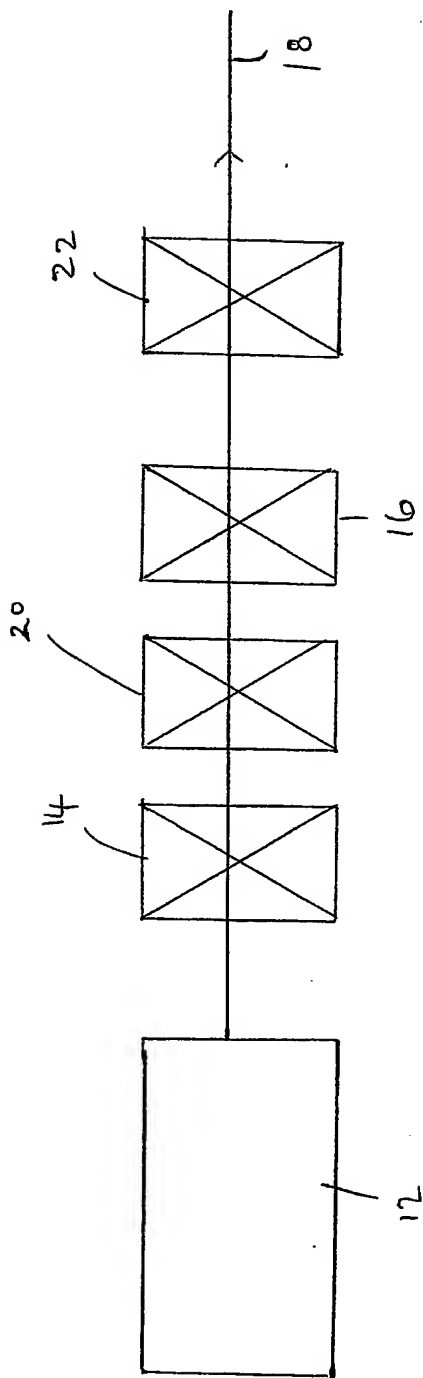


FIG. 1.

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Test Procedure

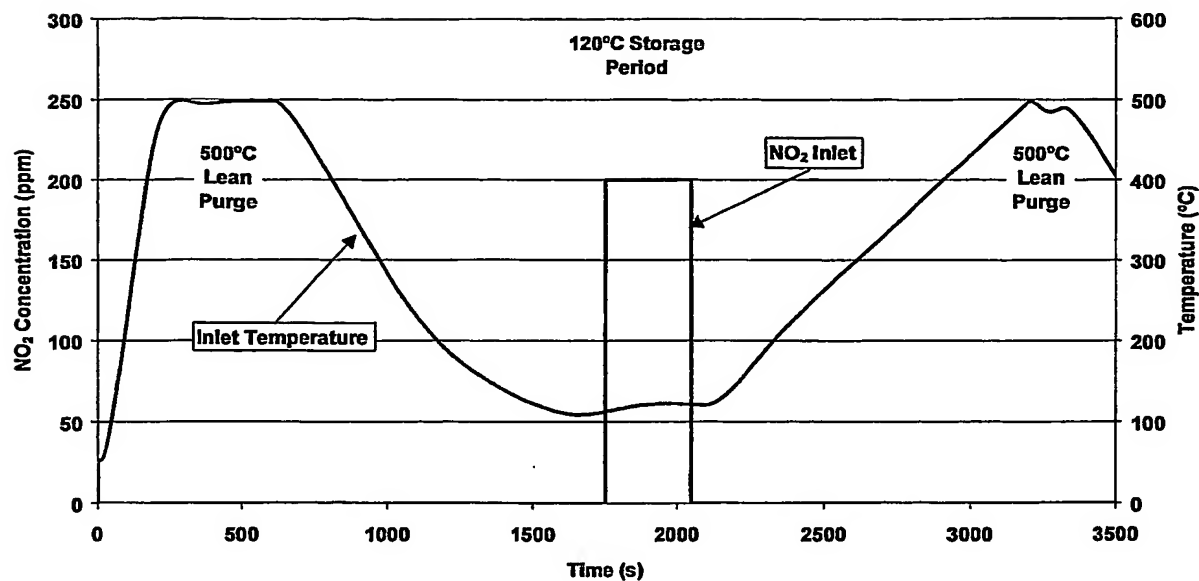


Fig 2.

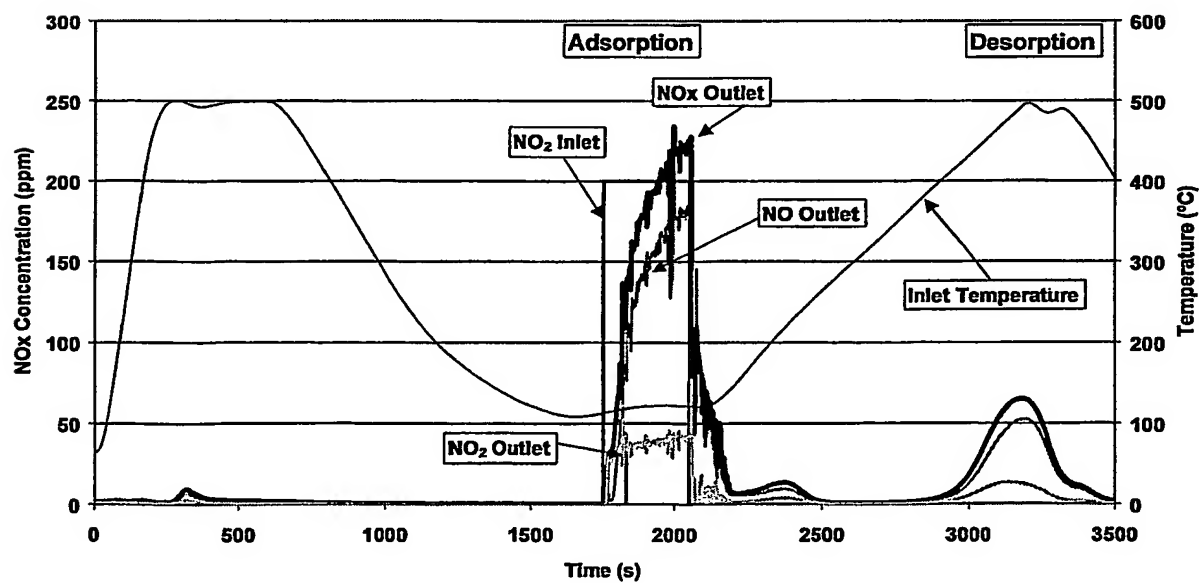
NO₂ Adsorption and Desorption for Conventional NO_x-Trap 120/5:0:1

Fig 3.

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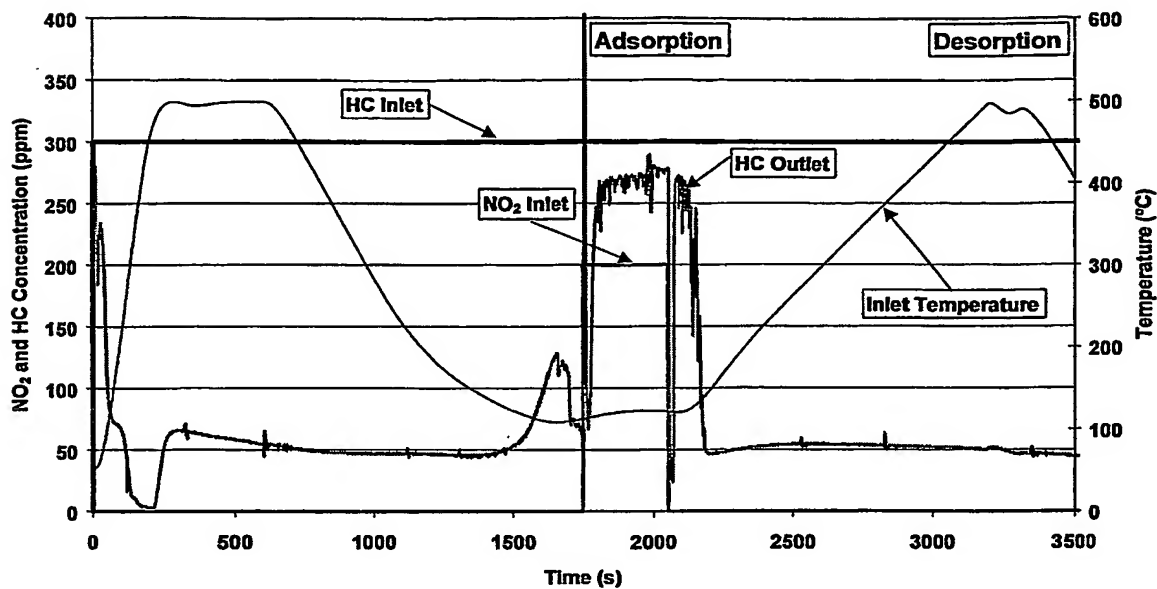
Outlet HC for Conventional NO_x-Trap 120/5:0:1

Fig 3A.

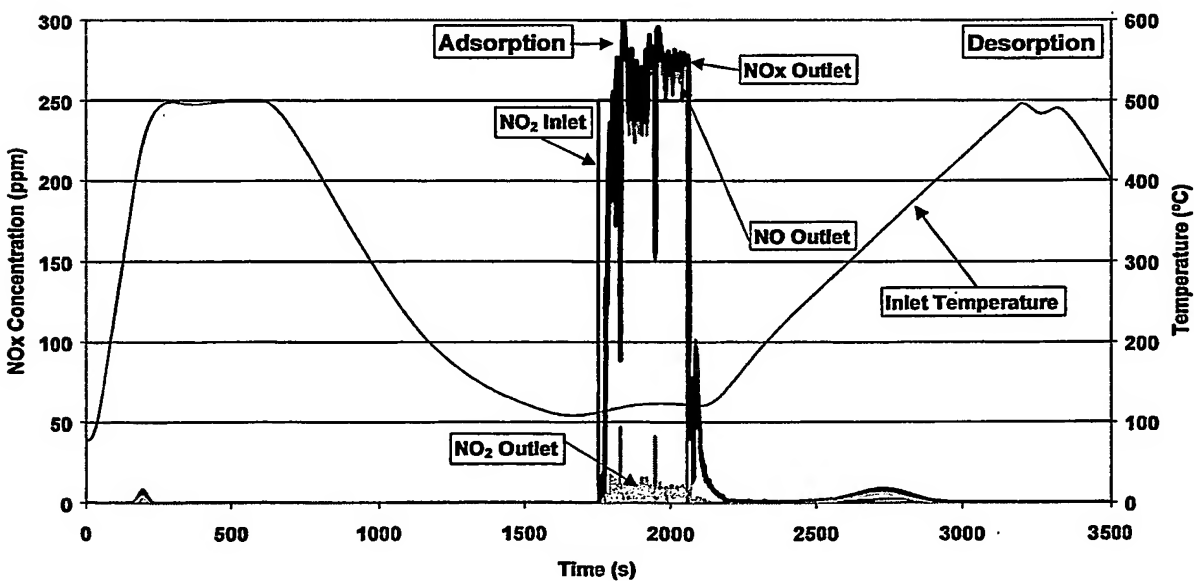
NO₂ Adsorption and Desorption for Pt Containing Washcoat

Fig 4.

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Outlet HC for Pt Containing Washcoat

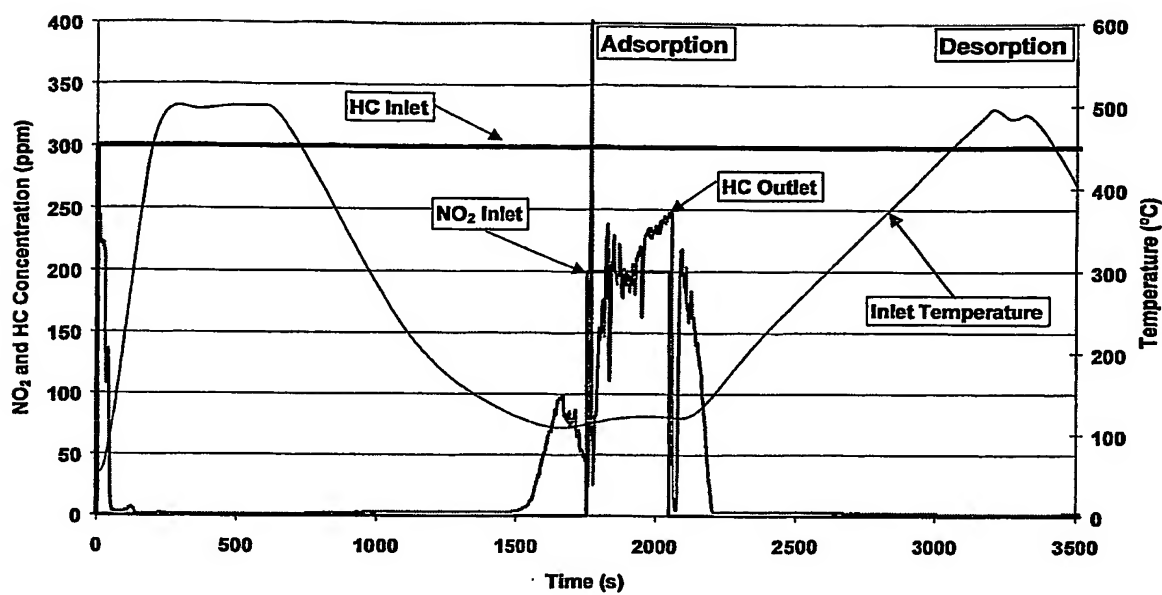


Fig 4A.

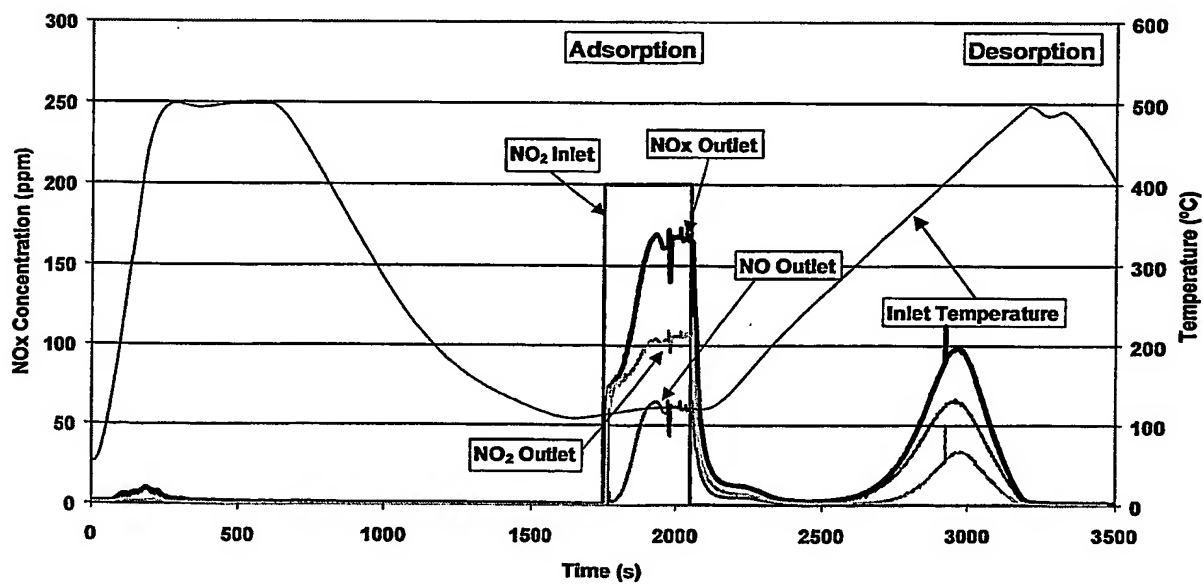
NO₂ Adsorption and Desorption for Washcoat minus Pt

Fig 5.

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Outlet HC for Washcoat minus Pt

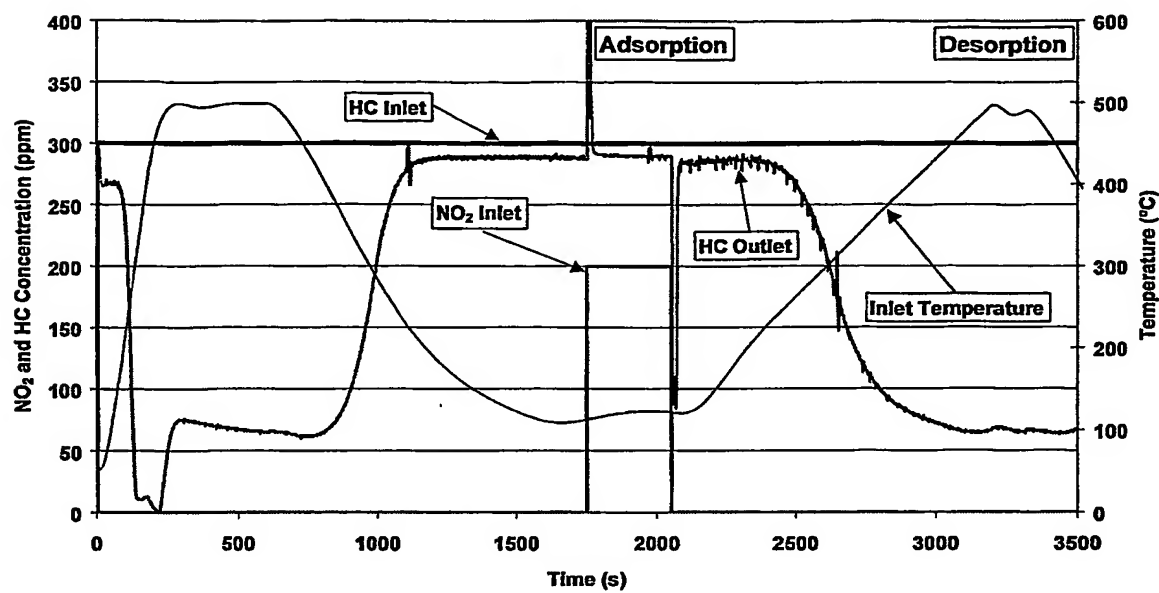


Fig 5A.

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/GB 03/04290

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D53/94 F01N3/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 893 154 A (VOLKSWAGENWERK AG) 27 January 1999 (1999-01-27) column 3, line 6 - line 53; figure 1 -----	1-8, 10, 11, 14-21
X	EP 0 814 242 A (JOHNSON MATTHEY PLC) 29 December 1997 (1997-12-29) column 3, line 26 - line 54 column 4, line 34 - line 42 column 5, line 25 - line 53 -----	1-8, 10, 11, 16-18, 20, 21
X	EP 1 101 908 A (VOLKSWAGENWERK AG) 23 May 2001 (2001-05-23) column 3, line 37 - column 5, line 18; figures 1-3 ----- -/-	1, 10, 12-14, 16-18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Eijkenboom, A

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/JP 03/04290

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/59611 A (ENGELHARD CORP) 12 October 2000 (2000-10-12) page 20, line 5 - page 22, line 27; claim 14; figures 2-4	1-8, 16-21
X	& WO 01/074476 A (ENGELHARD CORP) 11 October 2001 (2001-10-11) claim 1; figures 2-5 -----	1-8, 16-21

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